

# PATENT SPECIFICATION

DRAWINGS ATTACHED

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## COMPLETE SPECIFICATION

### A Water Treatment Process

We, KIMBERLY-CLARK CORPORATION, a corporation organized under the laws of the State of Delaware, United States of America, of Neenah, Wisconsin, United States of America do hereby declare the invention for which we pray that a patent may be granted to us and the method by which it is to be performed to be particularly described in and by the following statement.

10 This invention relates to a process for water reclamation. It is particularly directed to a system of water recirculation wherein make-up water is added only to the extent necessary to provide for incidental losses 15 which characterises the particular use to which the water is put.

Commonly, water for industrial use, is contaminated by, for example finely divided solids. In the case of some paper mill 20 effluent, for example, the finely divided solids include anionic material which may be in the form of fibrous particles. To remove the suspended solid material from the water, coagulants such as aluminium sulfate, iron 25 chloride and the like may be employed in conjunction with sedimentation and/or filtration procedures. The coagulants, and possibly, a coagulant aid, assist the building of a floc to a proper size for settling; sedimentation units may also be used to permit the 30 separation of the relatively slow settling floc thus formed, from the purified water.

In accordance with the invention a treatment process for water containing bicarbonate hardness comprises the steps of introducing to the water substantially unhydrated, finely divided magnesium oxide of a particle size which is less than 1 micron in the largest dimension to react the magnesium oxide 35 directly and essentially completely with the bicarbonate hardness (a) to provide the magnesium component in solution and (b) to decrease the bicarbonate hardness and there-

after adding to the water at least a sufficient amount of lime to precipitate the magnesium component as a coagulant.

The method of this invention affords a number of advantages. Particularly pertinent to industrial usages of the reclaimed water is that the procedure may be effected without the addition of comparatively refractory soluble salts to the system and, accordingly, there is no net increase in the dissolved solids of the water due to the water clarification treatment despite constant treatment and recirculation; in some instances, a decrease of dissolved solids may be achieved by removal in the primary softening step.

The method provides for a recirculation of 70% and more of the process water of 60 industrial systems. The magnesium oxide is preferably reacted with calcium bicarbonate hardness in the water up to a pH approximating 10.2 to produce magnesium carbonate and calcium carbonate with some minor 65 amount of magnesium bicarbonate normally resulting also. By effecting the reaction in the presence of make-up water or the water to be reclaimed, there is an initial softening of the water due to calcium carbonate formation. Thus, the reaction serves the purpose of softening and of providing the necessary soluble magnesium carbonate and/or bicarbonate for the primary softening treatment. Additionally, this reaction conserves lime by 70 virtue of the direct formation of the magnesium carbonate and calcium carbonate as principal reaction products. Importantly, also, the calcium carbonate constituent formed may be carried with the water to the 80 primary softening treatment to add weight to the sludge produced in this latter step, thus aiding settling.

Preferably the soluble magnesium salt has a relatively high pH occasioned by the lime 85 employed in this softening stage. Magnesium

hydroxide is formed *in situ* and effects a plurality of functions. First, it is a flocculent precipitate, essentially gelatinous and quite voluminous so that it readily encompasses even finely divided solids including calcium bearing compounds and substances in fibre form; some soluble organics also are absorbed by this gelatinous floc. Because of these floc characteristics we have found a coagulant aid to be desirable to effect coagulation into a dense relatively rapid settling sludge mass. Secondly, the formed magnesium hydroxide is effective to neutralize anionically charged particles, such as the fibre particles which, for example, a paper-making system effluent frequently contains; additionally, the positively charged magnesium hydroxide floc reduces the negative charge of calcium carbonate particles and of those coagulant aids which are normally negatively charged in aqueous solution. The addition of the magnesium salt for this latter purpose and the optional addition of cationic coagulant aids is effected to an extent that the zeta potential of the system in the primary softener is between about zero and  $\pm 5$  millivolts; in this range flocculation of the particles readily occurs. Thirdly, bacteria control is simultaneously achieved because of the high pH in the primary softener, about 10.5 to about 11.2, a condition under which the bacteria are destroyed. Fourthly, pollution control is also achieved since water normally discarded is reclaimable. The sludge occasioned by the magnesium hydroxide floc is readily separated from the water effluent, as by sedimentation.

The effluent of the primary treatment contains substantially only dissolved calcium carbonate, magnesium hydroxide, calcium hydroxide and soluble salts which may have originally present in the process water. Such effluent has the high pH range noted. This effluent is treated before stabilization to reduce the pH and to convert the magnesium and calcium hydroxide, at least in part, to magnesium and calcium carbonate. The presence of undissolved magnesium hydroxide is undesirable as it interferes with calcium carbonate crystal formation in the stabilization step.

Stabilization, that is, the removal of calcium carbonate supersaturation, could take place in the primary softener; however, we have found that with this present system usually only partial stabilization may be achieved in the primary softener and subsequent stabilization is essential.

This, we have found, is particularly influenced by the presence of phosphate ions in the water undergoing treatment. Such ions inhibit the controlled crystallization of the calcium carbonate resulting in a supersaturated solution. Such supersaturation must be removed to prevent calcium carbonate

deposition in the treating equipment as well as the equipment of the process for which the water is clarified.

The carbonated effluent is passed to the stabilizing unit with the calcium carbonate largely in supersaturated solution and its removal is achieved essentially by crystallization—facilitated by the incorporation of limestone in the form of fine particles into the stabilizing unit. The pH at this stabilization stage is preferably about 9.4 and suitably is in the range of 9.0 to 10.2.

Recarbonation of the effluent of the stabilizing unit results in the conversion of remaining magnesium and calcium components to soluble bicarbonates. Such water is preferably, but not necessarily, filtered and passed to the using system.

Make-up water to compensate for that lost in processing materials may be added to the system at various positions. The nature of the make-up water is, of course a factor but commonly the water is added to the preliminary reaction unit, the primary softener or first clarifier so that the water is treated as it is added. The water usually may also be added to the solids contacts stabilization unit. Depending upon process losses, a completely closed system may be maintained for long periods of time. For example, if there are only small losses or if care is taken to avoid or minimize losses by inhibiting evaporation, for example, the completely closed system is attained.

The sludge from the primary softener includes the magnesium hydroxide precipitate as well as the calcium carbonate, and other particle materials such as fibres. This sludge may be carbonated and the magnesium recovered as the soluble carbonate and bicarbonate. We have found, however, that in an economical system such may be dispensed with if magnesium oxide is employed as the magnesium source rather than more expensive salts. If dolomite is employed as the source of magnesium and/or lime, then magnesium recovery is necessary to recover the magnesium value of the dolomite. In some instances magnesium ions will be present in the make-up water and will reduce the magnesium component cost; however, we have found that it is usually necessary with naturally occurring waters to provide additional magnesium in some reactant form, particularly when magnesium content of the natural water is low or the make-up water is minimal.

The temperature conditions throughout the system are pertinent factors but will depend in considerable measure upon the nature of the system in which the clarified water is to be employed. Magnesium hydroxide floc, well hydrated, forms very readily at the required pH range at about 90 to 100°F. Many operations are carried out at such

temperatures and the effluent from a 'creped wadding machine, for example, is frequently in this range.

It is to be noted that the process thus broadly outlined does not of itself increase the dissolved solids of the water undergoing treatment. The water can therefore be re-used to an extent that is determined only by the water using process involved. If dissolved solids are introduced by the water using process, they may build up and limit water re-use.

The present invention, accordingly, employs magnesium hydroxide as a primary flocculent for suspended matter and is itself formed in situ from soluble magnesium carbonate, magnesium bicarbonate and mixtures thereof, the capacity of the magnesium hydroxide for flocculation being preferably 20 supplemented by the action of a coagulant aid to provide the necessary settling characteristics of the floc.

The water clarification treatment may be operable on a continuous basis, employing 25 normally essentially gelatinous and voluminous magnesium hydroxide precipitate as a primary flocculent and thus avoiding a net increase in dissolved soluble salts to the recirculating waters while achieving a high 30 per cent of water reclamation.

The invention will now be more fully described by way of example with reference to the accompanying drawings in which

Fig. 1 is a flow chart illustrating the steps 35 in a preferred embodiment of the process of the invention with optional steps designated and as applied to papermaking water reclamation; and

Fig. 2 is a flow chart illustrating a system 40 for magnesium recovery and the attainment of a dry sludge.

While the procedure of invention is applicable to the treatment of water for many uses, particularly industrial use, the process will 45 be particularly described in connection with water used in a paper mill.

In the drawing the numeral 1 designates a flow path for effluent from a paper mill. Such effluent may commonly contain fibre particles 50 in suspension together with dissolved calcium bicarbonate, magnesium carbonate and bicarbonate as well as surfactants such as the phosphates, for example, sodium hexameta-phosphate. Additionally, the original water 55 supply may contain varying amounts of impurities such as organic matter from decaying vegetation, inorganic dissolved components such as chlorides, sulphates, carbonates of calcium, magnesium and sodium as well as oxides of iron, aluminium and silica, and also dissolved gases; some of such constituents may be included in the effluent and may not be detrimental to the particular process. Generally, however, salts 60 of iron are eliminated to avoid paper dis-

colouration and the organics induce slime formation and must be precluded. By the procedure described hereinafter, aluminium oxide, silica if present, and carbonates are removed as well as the iron and organic 70 components. Chlorides and sulphates may be limited if necessary to the process either by de-ionization equipment or by bleed-off from the process effluent while still recirculating at least 70% of the water. 75

The effluent flow path 1 communicates with a reaction zone to which finely divided, substantially unhydrated magnesium oxide is supplied. Carbon dioxide may also be supplied as required to form carbonic acid for 80 reaction with the magnesium oxide. Any device which permits of addition and thorough mixing of the constituents and provides for sludge and effluent withdrawal is suitable for the purpose of this mixing zone. 85 The magnesium oxide utilised in this embodiment of the invention is provided finely divided in an aqueous slurry to facilitate its solution and reaction with carbonic acid and calcium and magnesium bicarbonate present. 90 The carbon dioxide, if required for solution of the necessary amount of magnesium oxide, may be from any convenient source such as boiler stack gases. The bicarbonate may be a constituent of the re-cycled water and/or 95 the make-up water. The magnesium oxide is added in sufficient quantity to provide for flocculation and, if practical, a pH in the reaction zone approaching 10.2; the pH should not be less than about 8.3 to provide 100 a predominance of calcium and magnesium carbonates which require less lime for precipitation. Make-up water is commonly added to the reaction zone as necessary to provide for system usage or losses. Primary 105 products of this reaction are magnesium carbonate in solution and calcium carbonate as a precipitate or in supersaturated solution. Optionally, this calcium carbonate may be eliminated by settling and withdrawal 110 through path 2 or may be passed to the primary softening zone through a path designated at 3. I have found that the latter procedure is beneficial to the softening step as it aids settling of the floc. 115

The softener is preferably an upflow clarifier although it may be any unit which provides agitation and permits separation of sludge from a primary effluent. The necessary lime and coagulant aid (about 0.1 to 1 p.p.m.) 120 are introduced to the clarifier as indicated, together with make-up water as required, and withdrawal of sludge-free effluent is through flow path 4. The sludge passes out through path 5 to waste or for recovery of 125 the magnesium constituent if such is desired. The coagulant aid influences the zeta potential and is selected to aid achievement of a zeta potential of 0 +5 millivolts in the particular system. The coagulant aids commer- 130

cially available are suitable and include locust bean gum, sodium alginate, synthetic polymers, i.e. Separan (Registered Trade Mark), a commercial high molecular weight 5 polyacrylamide and a product of Dow Chemical Company, Midland, Michigan.

The magnesium hydroxide is formed in the primary softener from the carbonate in situ in the presence of the high pH (at least 10.2 to and preferably 10.5) induced by the lime addition to the softening zone. This pH 10 may suitably be as high as 11.2 where bacteria, control is necessary. The influent 15 through flow path 3 is suitably about 90°F.; this temperature has no significant limit but at higher temperatures the reaction is faster and, of course, the temperature and pressure 20 conditions should be such that the system is liquid. The make-up water itself constitutes 25 not more than about 25% by weight of the primary softener fluid contents.

Alternatively, the effluent may initially be directed to the softening zone through path 3a and the soluble magnesium salts specified 25 are then supplied to this zone.

The primary softener effluent flow path 4 communicates with a carbonation zone. Carbon dioxide is introduced into the effluent in this zone to eliminate hydroxyl 30 ions and to lower the pH such that the system has a pH of between about 9.0 to 10.2 in the subsequent stabilization zone. The effluent of this carbonation zone passes through path 6 to the solids contact 35 stabilization zone. The carbonation zone effluent contains some magnesium ions, carbonate ions, and, more particularly, calcium carbonate in supersaturated solution. The magnesium ions in this paper 40 making system will have no deleterious effect on papermaking operations and, accordingly, may be passed through the cycle and will serve to reduce the quantity of magnesium oxide introduced into the reaction 45 zone. Therefore, it is not essential that magnesium components be reduced below that point at which they might precipitate in subsequent operations, that is, other than the precipitation in the primary softener.

50 The stabilization zone is suitably an upflow clarifier also. The zone is seeded with crushed limestone of a particle size preferably in the range of 35 microns to 50 microns. The pH in this zone as noted is about 9.0 to 10.2. 55 Preferably, the pH is maintained at about 9.4 for optimum calcium carbonate precipitation. Particle size of the calcium carbonate precipitated is maintained in desired size range by the inclusion of a coagulant aid to the 60 extent of about 0.1 to 5 p.p.m. Such is not always necessary but is effective to agglomerate particles fractured from the seed particles. The pH is controlled by prior addition of carbon dioxide. Under these conditions, much of the magnesium components

will remain in solution. The effluent of this stabilization zone should contain not more than about 25 to 35 p.p.m. residual alkalinity. The stabilization unit is preferably selected so that the calcium carbonate precipitating from the upflowing liquid will be hydraulically graded—the coarser material being selectively passed toward the path 7 to waste while the finer material is retained in suspension in the treated water. Stabilization 75 is suitably accomplished by maintaining about 1 to 10% by weight of the material of the stabilization zone as suspended solids at a rise rate of about 1.5 gallons per ft. squared per minute.

The effluent of the stabilization zone for papermaking purposes is directed through the path indicated at 8 and re-carbonated to lower the pH to about 8.3 and below, usually not lower than 6.0; it is then passed through 85 path 9 to a filtration zone such as a diatomite filtration procedure, if so desired. The necessity for recarbonation is dependent upon the specific nature of the process in which the clarified water is employed.

The filtered water containing dissolved calcium components as well as some dissolved magnesium components passes to the paper mill system through path 10 and, after use, is returned for reprocessing through 95 path 1.

Important to the described procedure is the requirement that the lime addition raise the pH to within the range of 10.2 to 11.2 and that the magnesium oxide addition be sufficient to provide coagulation in the primary softening step and to adjust the zeta potential toward the range of  $0 \pm 5$  millivolts. The coagulant aids may be anionic or cationic and, as stated above, are selected to provide 100 the system in the noted zeta potential range. Of further importance is the reduction of the stabilized effluent to a condition that the magnesium and the calcium components are 105 present as the bicarbonates.

To minimize water losses, to provide for economy in the use of magnesium, and, importantly, to achieve a dry sludge which may be subject to ready disposal, the procedure illustrated in Fig. 2 may be followed. 115 Specifically, the sludge and recovered precipitates of the procedure of Fig. 1 are recarbonated and then subjected to a solids separation. The magnesium component in solution as the bicarbonate is directed to the 120 softening zone (Fig. 1). The dry sludge is directed to waste. The utilization of such procedure is desirable in those instances where the magnesium cost is high and wet sludge disposal is a particular problem. The 125 solids separation is effected by any suitable means such as filtration or centrifugal action.

#### WHAT WE CLAIM IS:—

1. A treatment process for water containing bicarbonate hardness comprising the 130

steps of introducing to the water substantially unhydrated, finely divided magnesium oxide of a particle size which is less than 1 micron in the largest dimension to react the magnesium oxide directly and essentially completely with the bicarbonate hardness a) to provide the magnesium component in solution as magnesium carbonate and b) to decrease the bicarbonate hardness, and 5 thereafter adding to the water at least a sufficient amount of lime to precipitate the magnesium component as a coagulant.

2. A process as claimed in Claim 1 in which the water containing the bicarbonate hardness is recirculated water of a water using process.

3. A process as claimed in Claim 1 in which the water containing the bicarbonate hardness is makeup water for a recirculation 10 water process.

4. A process as claimed in Claim 1 comprising the steps of

a) feeding water to be reclaimed to a reaction zone and reacting the bicarbonate hardness 15 with substantially unhydrated, finely divided magnesium oxide of a particle size which is less than 1 micron in the largest dimension such that the magnesium oxide reacts directly to produce magnesium carbonate in solution

30 b) and to reduce the bicarbonate hardness;

c) admixing with the water containing the magnesium carbonate sufficient lime to provide a pH in the range of about 10.2 to 11.2 and to provide in situ formation of a gelatinous, voluminous flocculent precipitate of magnesium hydroxide;

35 d) coagulating by agitating the water to cause the flocculent precipitate to encompass suspended matter and to form a sludge there-with;

e) passing the sludge resulting from the coagulation along a path by which the sludge is eliminated from the effluent water;

40 f) passing the effluent water along a main flow path and carbonating the effluent water to reduce the pH to between about 9.0 to 10.2 and to convert hydroxides in the effluent to carbonates;

45 g) stabilizing the carbonated effluent by contact with finely divided calcium carbonate particles whereby any calcium carbonate in supersaturated solution is precipitated and the water is clarified;

50 h) continuously recirculating the effluent from the using process through the said steps from the reaction zone and back to the using process.

5. A process as claimed in claim 1 comprising the steps of

a) feeding water to be reclaimed and substantially unhydrated, finely divided magnesium oxide of a particle size which is less than 1 micron in the largest dimension to a reaction zone to achieve a pH of at least 8.3 and up to 10.2 to form by direct reaction of calcium bicarbonate hardness and the magnesium oxide, calcium carbonate and to provide the magnesium component essentially as magnesium carbonate in solution;

b) flowing effluent of step a) to a softening zone and admixing the said effluent with a coagulant aid and sufficient lime to provide a pH in the range of 10.2 to 11.2 and to provide in situ formation of a gelatinous, voluminous, flocculent precipitate of magnesium hydroxide and a zeta potential of  $0 \pm 5$  millivolts;

c) coagulating by agitating the water to cause the flocculent precipitate to encompass suspended matter and form a sludge there-with;

d) passing the sludge resulting from the coagulation along a path by which the sludge is eliminated from the effluent water;

e) passing the effluent water along a main flow path and carbonating the effluent water to reduce the pH and to convert hydroxides in the effluent to carbonates;

f) stabilizing the carbonated effluent at a pH of 9.0 to 10.2 by contact with finely divided calcium carbonate particles whereby any calcium carbonate in supersaturated solution is precipitated and the water is clarified;

g) circulating the water so clarified to a water using process from which at least 70% of the water is recoverable as an effluent; and

h) continuously recirculating the effluent from the using process through the said steps and back to the using process.

6. A process substantially as hereinbefore described with reference to the accompanying drawings.

For the Applicants:  
 LLOYD WISE, BOULY & HAIG,  
 Chartered Patent Agents,  
 Norman House,  
 105-109 Strand,  
 London, W.C.2.

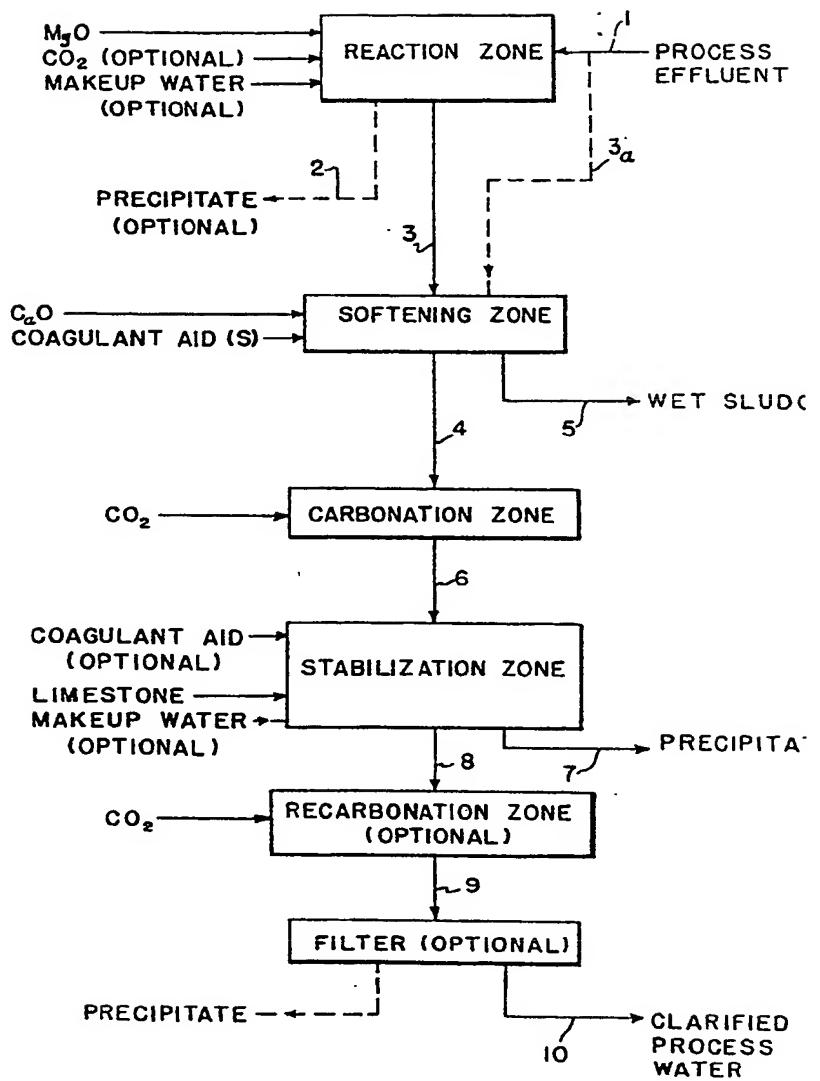


FIG. I

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COMPLETE SPECIFICATION

2 SHEETS

*This drawing is a reproduction of  
the Original on a reduced scale  
Sheets 1 & 2*

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CIPITATE

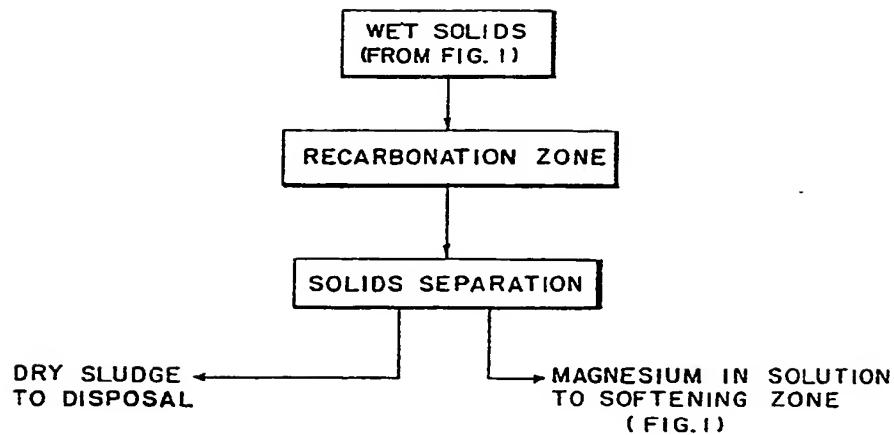


FIG. 2

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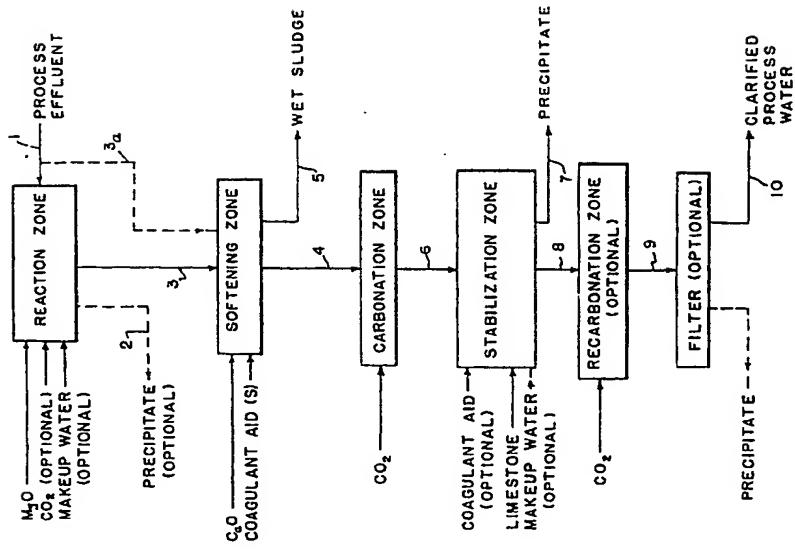


FIG. 2

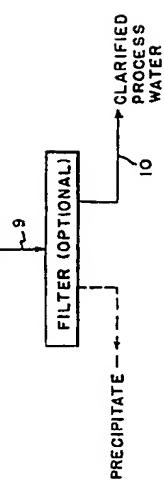


FIG. 1

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Commonly, water for industrial use, is contaminated by, for example finely divided solids. In the case of some paper mill 20 effluent, for example, the finely divided solids include anionic material which may be in the form of fibrous particles. To remove the suspended solid material from the water, coagulants such as aluminium sulfate, iron 25 chloride and the like may be employed in conjunction with sedimentation and/or filtration procedures. The coagulants, and possibly, a coagulant aid, assist the building of a floc to a proper size for settling; sedimentation units may also be used to permit the 30 separation of the relatively slow settling floc thus formed, from the purified water.

In accordance with the invention a treatment process for water containing bicarbonate hardness comprises the steps of introducing to the water substantially unhydrated, finely divided magnesium oxide of a particle size which is less than 1 micron in the largest dimension to react the magnesium oxide 35 directly and essentially completely with the bicarbonate hardness (a) to provide the magnesium component in solution and (b) to decrease the bicarbonate hardness and there-

after adding to the water at least a sufficient amount of lime to precipitate the magnesium component as a coagulant.

The method of this invention affords a number of advantages. Particularly pertinent to industrial usages of the reclaimed water is that the procedure may be effected without the addition of comparatively refractory soluble salts to the system and, accordingly, there is no net increase in the dissolved solids of the water due to the water clarification treatment despite constant treatment and recirculation; in some instances, a decrease of dissolved solids may be achieved by removal in the primary softening step.

The method provides for a recirculation of 70% and more of the process water of industrial systems. The magnesium oxide is preferably reacted with calcium bicarbonate hardness in the water up to a pH approximating 10.2 to produce magnesium carbonate and calcium carbonate with some minor amount of magnesium bicarbonate normally resulting also. By effecting the reaction in the presence of make-up water or the water to be reclaimed, there is an initial softening of the water due to calcium carbonate formation. Thus, the reaction serves the purpose of softening and of providing the necessary soluble magnesium carbonate and/or bicarbonate for the primary softening treatment. Additionally, this reaction conserves lime by virtue of the direct formation of the magnesium carbonate and calcium carbonate as principal reaction products. Importantly, also, the calcium carbonate constituent formed may be carried with the water to the primary softening treatment to add weight to the sludge produced in this latter step, thus aiding settling.

Preferably the soluble magnesium salt has a relatively high pH occasioned by the lime employed in this softening stage. Magnesium

hydroxide is formed *in situ* and effects a plurality of functions. First, it is a flocculent precipitate, essentially gelatinous and quite voluminous so that it readily encompasses even finely divided solids including calcium bearing compounds and substances in fibre form; some soluble organics also are absorbed by this gelatinous floc. Because of these floc characteristics we have found a coagulant aid to be desirable to effect coagulation into a dense relatively rapid settling sludge mass. Secondly, the formed magnesium hydroxide is effective to neutralize anionically charged particles, such as the fibre particles which, for example, a paper-making system effluent frequently contains; additionally, the positively charged magnesium hydroxide floc reduces the negative charge of calcium carbonate particles and of those coagulant aids which are normally negatively charged in aqueous solution. The addition of the magnesium salt for this latter purpose and the optional addition of cationic coagulant aids is effected to an extent that the zeta potential of the system in the primary softener is between about zero and  $\pm 5$  millivolts; in this range flocculation of the particles readily occurs. Thirdly, bacteria control is simultaneously achieved because of the high pH in the primary softener, about 10.5 to about 11.2, a condition under which the bacteria are destroyed. Fourthly, pollution control is also achieved since water normally discarded is reclaimable. The sludge occasioned by the magnesium hydroxide floc is readily separated from the water effluent, as by sedimentation.

The effluent of the primary treatment contains substantially only dissolved calcium carbonate, magnesium hydroxide, calcium hydroxide and soluble salts which may have originally present in the process water. Such effluent has the high pH range noted. This effluent is treated before stabilization to reduce the pH and to convert the magnesium and calcium hydroxide, at least in part, to magnesium and calcium carbonate. The presence of undissolved magnesium hydroxide is undesirable as it interferes with calcium carbonate crystal formation in the stabilization step.

Stabilization, that is, the removal of calcium carbonate supersaturation, could take place in the primary softener; however, we have found that with this present system usually only partial stabilization may be achieved in the primary softener and subsequent stabilization is essential.

This, we have found, is particularly influenced by the presence of phosphate ions in the water undergoing treatment. Such ions inhibit the controlled crystallization of the calcium carbonate resulting in a supersaturated solution. Such supersaturation must be removed to prevent calcium carbonate

deposition in the treating equipment as well as the equipment of the process for which the water is clarified.

The carbonated effluent is passed to the stabilizing unit with the calcium carbonate largely in supersaturated solution and its removal is achieved essentially by crystallization—facilitated by the incorporation of limestone in the form of fine particles into the stabilizing unit. The pH at this stabilization stage is preferably about 9.4 and suitably is in the range of 9.0 to 10.2.

Recarbonation of the effluent of the stabilizing unit results in the conversion of remaining magnesium and calcium components to soluble bicarbonates. Such water is preferably, but not necessarily, filtered and passed to the using system.

Make-up water to compensate for that lost in processing materials may be added to the system at various positions. The nature of the make-up water is, of course, a factor but commonly the water is added to the preliminary reaction unit, the primary softener or first clarifier so that the water is treated as it is added. The water usually may also be added to the solids contacts stabilization unit. Depending upon process losses, a completely closed system may be maintained for long periods of time. For example, if there are only small losses or if care is taken to avoid or minimize losses by inhibiting evaporation, for example, the completely closed system is attained.

The sludge from the primary softener includes the magnesium hydroxide precipitate as well as the calcium carbonate, and other particle materials such as fibres. This sludge may be carbonated and the magnesium recovered as the soluble carbonate and bicarbonate. We have found, however, that in an economical system such may be dispensed with if magnesium oxide is employed as the magnesium source rather than more expensive salts. If dolomite is employed as the source of magnesium and/or lime, then magnesium recovery is necessary to recover the magnesium value of the dolomite. In some instances magnesium ions will be present in the make-up water and will reduce the magnesium component cost; however, we have found that it is usually necessary with naturally occurring waters to provide additional magnesium in some reactant form, particularly when magnesium content of the natural water is low or the make-up water is minimal.

The temperature conditions throughout the system are pertinent factors but will depend in considerable measure upon the nature of the system in which the clarified water is to be employed. Magnesium hydroxide floc, well hydrated, forms very readily at the required pH range at about 90 to 100°F. Many operations are carried out at such

temperatures and the effluent from a 'creped' wadding machine, for example, is frequently in this range.

It is to be noted that the process thus broadly outlined does not of itself increase the dissolved solids of the water undergoing treatment. The water can therefore be re-used to an extent that is determined only by the water using process involved. If dissolved solids are introduced by the water using process, they may build up and limit water re-use.

The present invention, accordingly, employs magnesium hydroxide as a primary flocculent for suspended matter and is itself formed in situ from soluble magnesium carbonate, magnesium bicarbonate and mixtures thereof, the capacity of the magnesium hydroxide for flocculation being preferably supplemented by the action of a coagulant aid to provide the necessary settling characteristics of the floc.

The water clarification treatment may be operable on a continuous basis, employing 25 normally essentially gelatinous and voluminous magnesium hydroxide precipitate as a primary flocculent and thus avoiding a net increase in dissolved soluble salts to the 30 recirculating waters while achieving a high per cent of water reclamation.

The invention will now be more fully described by way of example with reference to the accompanying drawings in which

35 Fig. 1 is a flow chart illustrating the steps in a preferred embodiment of the process of the invention with optional steps designated and as applied to papermaking water reclamation; and

Fig. 2 is a flow chart illustrating a system for magnesium recovery and the attainment of a dry sludge.

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55 supply may contain varying amounts of impurities such as organic matter from decaying vegetation, inorganic dissolved components such as chlorides, sulphates, carbonates of calcium, magnesium and 60 sodium as well as oxides of iron, aluminium and silica, and also dissolved gases; some of such constituents may be included in the effluent and may not be detrimental to the particular process. Generally, however, salts 65 of iron are eliminated to avoid paper dis-

colouration and the organics induce slime formation and must be precluded. By the procedure described hereinafter, aluminium oxide, silica if present, and carbonates are removed as well as the iron and organic 70 components. Chlorides and sulphates may be limited if necessary to the process either by de-ionization equipment or by bleed-off from the process effluent while still recirculating at least 70% of the water.

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The effluent flow path 1 communicates with a reaction zone to which finely divided, substantially unhydrated magnesium oxide is supplied. Carbon dioxide may also be supplied as required to form carbonic acid for reaction with the magnesium oxide. Any device which permits of addition and thorough mixing of the constituents and provides for sludge and effluent withdrawal is suitable for the purpose of this mixing zone. 85 The magnesium oxide utilised in this embodiment of the invention is provided finely divided in an aqueous slurry to facilitate its solution and reaction with carbonic acid and calcium and magnesium bicarbonate present. 90 The carbon dioxide, if required for solution of the necessary amount of magnesium oxide, may be from any convenient source such as boiler stack gases. The bicarbonate may be a constituent of the re-cycled water and/or 95 the make-up water. The magnesium oxide is added in sufficient quantity to provide for flocculation and, if practical, a pH in the reaction zone approaching 10.2; the pH should not be less than about 8.3 to provide 100 a predominance of calcium and magnesium carbonates which require less lime for precipitation. Make-up water is commonly added to the reaction zone as necessary to provide for system usage or losses. Primary 105 products of this reaction are magnesium carbonate in solution and calcium carbonate as a precipitate or in supersaturated solution. Optionally, this calcium carbonate may be eliminated by settling and withdrawal 110 through path 2 or may be passed to the primary softening zone through a path designated at 3. I have found that the latter procedure is beneficial to the softening step as it aids settling of the floc. 115

The softener is preferably an upflow clarifier although it may be any unit which provides agitation and permits separation of sludge from a primary effluent. The necessary lime and coagulant aid (about 0.1 to 1 p.p.m.) are introduced to the clarifier as indicated, together with make-up water as required, and withdrawal of sludge-free effluent is through flow path 4. The sludge passes out through path 5 to waste or for recovery of the magnesium constituent if such is desired. The coagulant aid influences the zeta potential and is selected to aid achievement of a zeta potential of  $0 \pm 5$  millivolts in the particular system. The coagulant aids commer- 125 130

cially available are suitable and include locust bean gum, sodium alginate, synthetic polymers, i.e. Separan (Registered Trade Mark), a commercial high molecular weight 5 polyacrylamide and a product of Dow Chemical Company, Midland, Michigan.

The magnesium hydroxide is formed in the primary softener from the carbonate in situ in the presence of the high pH (at least 10.2 to and preferably 10.5) induced by the lime addition to the softening zone. This pH 10 may suitably be as high as 11.2 where bacteria, control is necessary. The influent 15 through flow path 3 is suitably about 90°F.; this temperature has no significant limit but at higher temperatures the reaction is faster and, of course, the temperature and pressure 20 conditions should be such that the system is liquid. The make-up water itself constitutes not more than about 25% by weight of the 25 primary softener fluid contents.

Alternatively, the effluent may initially be directed to the softening zone through path 3a and the soluble magnesium salts specified 25 are then supplied to this zone.

The primary softener effluent flow path 4 communicates with a carbonation zone. Carbon dioxide is introduced into the effluent in this zone to eliminate hydroxyl 30 ions and to lower the pH such that the system has a pH of between about 9.0 to 10.2 in the subsequent stabilization zone. The effluent of this carbonation zone passes through path 6 to the solids contact 35 stabilization zone. The carbonation zone effluent contains some magnesium ions, carbonate ions, and, more particularly, calcium carbonate in supersaturated solution. The magnesium ions in this paper 40 making system will have no deleterious effect on papermaking operations and, accordingly, may be passed through the cycle and will serve to reduce the quantity of magnesium oxide introduced into the reaction 45 zone. Therefore, it is not essential that magnesium components be reduced below that point at which they might precipitate in subsequent operations, that is, other than the precipitation in the primary softener.

50 The stabilization zone is suitably an upflow clarifier also. The zone is seeded with crushed limestone of a particle size preferably in the range of 35 microns to 50 microns. The pH in this zone as noted is about 9.0 to 10.2. 55 Preferably, the pH is maintained at about 9.4 for optimum calcium carbonate precipitation. Particle size of the calcium carbonate precipitated is maintained in desired size range by the inclusion of a coagulant aid to the 60 extent of about 0.1 to 5 p.p.m. Such is not always necessary but is effective to agglomerate particles fractured from the seed particles. The pH is controlled by prior addition of carbon dioxide. Under these conditions, much of the magnesium components

will remain in solution. The effluent of this stabilization zone should contain not more than about 25 to 35 p.p.m. residual alkalinity. The stabilization unit is preferably selected so that the calcium carbonate precipitating from the upflowing liquid will be hydraulically graded—the coarser material being selectively passed toward the path 7 to waste while the finer material is retained in suspension in the treated water. Stabilization 70 is suitably accomplished by maintaining about 1 to 10% by weight of the material of the stabilization zone as suspended solids at a rise rate of about 1.5 gallons per ft. squared per minute. 80

The effluent of the stabilization zone for papermaking purposes is directed through the path indicated at 8 and re-carbonated to lower the pH to about 8.3 and below, usually not lower than 6.0; it is then passed through path 9 to a filtration zone such as a diatomite filtration procedure, if so desired. The necessity for re-carbonation is dependent upon the specific nature of the process in which the 85 clarified water is employed. 90

The filtered water containing dissolved calcium components as well as some dissolved magnesium components passes to the paper mill system through path 10 and, after use, is returned for reprocessing through 95 path 1.

Important to the described procedure is the requirement that the lime addition raise the pH to within the range of 10.2 to 11.2 and that the magnesium oxide addition be sufficient to provide coagulation in the primary softening step and to adjust the zeta potential toward the range of  $0 \pm 5$  millivolts. The coagulant aids may be anionic or cationic and, as stated above, are selected to provide 100 the system in the noted zeta potential range. Of further importance is the reduction of the 105 stabilized effluent to a condition that the magnesium and the calcium components are present as the bicarbonates. 110

To minimize water losses, to provide for economy in the use of magnesium, and, importantly, to achieve a dry sludge which may be subject to ready disposal, the procedure illustrated in Fig. 2 may be followed. 115 Specifically, the sludge and recovered precipitates of the procedure of Fig. 1 are re-carbonated and then subjected to a solids separation. The magnesium component in solution as the bicarbonate is directed to the 120 softening zone (Fig. 1). The dry sludge is directed to waste. The utilization of such procedure is desirable in those instances where the magnesium cost is high and wet 125 sludge disposal is a particular problem. The solids separation is effected by any suitable means such as filtration or centrifugal action.

#### WHAT WE CLAIM IS:—

1. A treatment process for water containing bicarbonate hardness comprising the 130

steps of introducing to the water substantially unhydrated, finely divided magnesium oxide of a particle size which is less than 1 micron in the largest dimension to react the magnesium oxide directly and essentially completely with the bicarbonate hardness a) to provide the magnesium component in solution as magnesium carbonate and b) to decrease the bicarbonate hardness, and thereafter adding to the water at least a sufficient amount of lime to precipitate the magnesium component as a coagulant.

2. A process as claimed in Claim 1 in which the water containing the bicarbonate hardness is recirculated water of a water using process.

3. A process as claimed in Claim 1 in which the water containing the bicarbonate hardness is makeup water for a recirculation water process.

4. A process as claimed in Claim 1 comprising the steps of

a) feeding water to be reclaimed to a reaction zone and reacting the bicarbonate hardness with substantially unhydrated, finely divided magnesium oxide of a particle size which is less than 1 micron in the largest dimension such that the magnesium oxide reacts directly to produce magnesium carbonate in solution and to reduce the bicarbonate hardness;

b) admixing with the water containing the magnesium carbonate sufficient lime to provide a pH in the range of about 10.2 to 11.2 and to provide in situ formation of a gelatinous, voluminous, flocculent precipitate of magnesium hydroxide;

c) coagulating by agitating the water to cause the flocculent precipitate to encompass suspended matter and to form a sludge therewith;

d) passing the sludge resulting from the coagulation along a path by which the sludge is eliminated from the effluent water;

e) passing the effluent water along a main flow path and carbonating the effluent water to reduce the pH to between about 9.0 to 10.2 and to convert hydroxides in the effluent to carbonates;

f) stabilizing the carbonated effluent by contact with finely divided calcium carbonate particles whereby any calcium carbonate in supersaturated solution is precipitated and the water is clarified;

g) circulating the water so clarified to a water using process from which at least 70% of the water is recoverable as an effluent; and

h) continuously recirculating the effluent from the using process through the said steps from the reaction zone and back to the using process.

5. A process as claimed in claim 1 comprising the steps of

a) feeding water to be reclaimed and substantially unhydrated, finely divided magnesium oxide of a particle size which is less than 1 micron in the largest dimension to a reaction zone to achieve a pH of at least 8.3 and up to 10.2 to form by direct reaction of calcium bicarbonate hardness and the magnesium oxide, calcium carbonate and to provide the magnesium component essentially as magnesium carbonate in solution;

b) flowing effluent of step a) to a softening zone and admixing the said effluent with a coagulant aid and sufficient lime to provide a pH in the range of 10.2 to 11.2 and to provide in situ formation of a gelatinous, voluminous, flocculent precipitate of magnesium hydroxide and a zeta potential of  $0 \pm 5$  millivolts;

c) coagulating by agitating the water to cause the flocculent precipitate to encompass suspended matter and form a sludge therewith;

d) passing the sludge resulting from the coagulation along a path by which the sludge is eliminated from the effluent water;

e) passing the effluent water along a main flow path and carbonating the effluent water to reduce the pH and to convert hydroxides in the effluent to carbonates;

f) stabilizing the carbonated effluent at a pH of 9.0 to 10.2 by contact with finely divided calcium carbonate particles whereby any calcium carbonate in supersaturated solution is precipitated and the water is clarified;

g) circulating the water so clarified to a water using process from which at least 70% of the water is recoverable as an effluent; and

h) continuously recirculating the effluent from the using process through the said steps and back to the using process.

6. A process substantially as hereinbefore described with reference to the accompanying drawings.

For the Applicants:  
 LLOYD WISE, BOULY & HAIG,  
 Chartered Patent Agents,  
 Norman House,  
 105-109 Strand,  
 London, W.C.2.

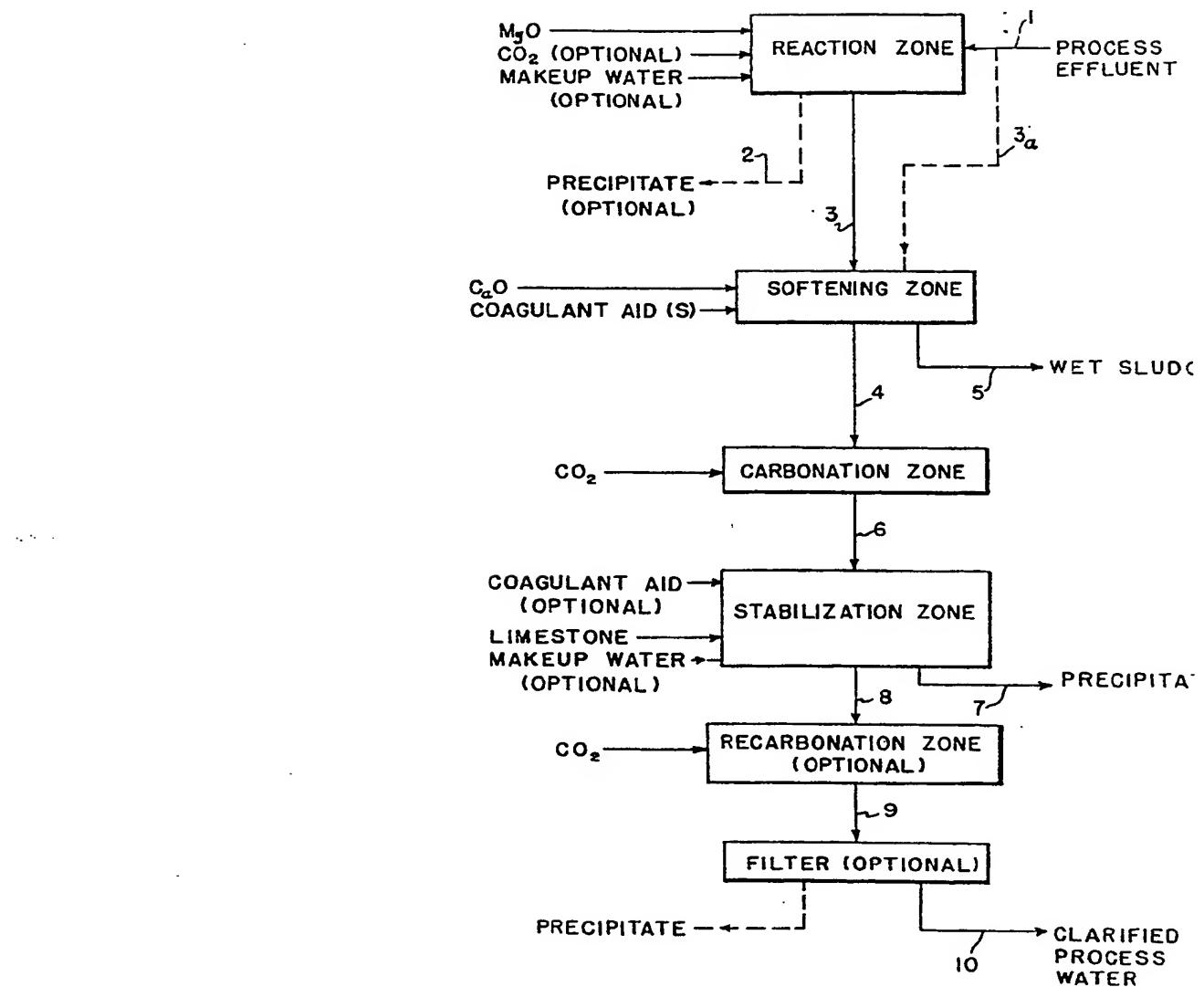


FIG. I

1090822

COMPLETE SPECIFICATION

2 SHEETS

*This drawing is a reproduction of  
the Original on a reduced scale  
Sheets 1 & 2*

CESS  
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SLUDGE

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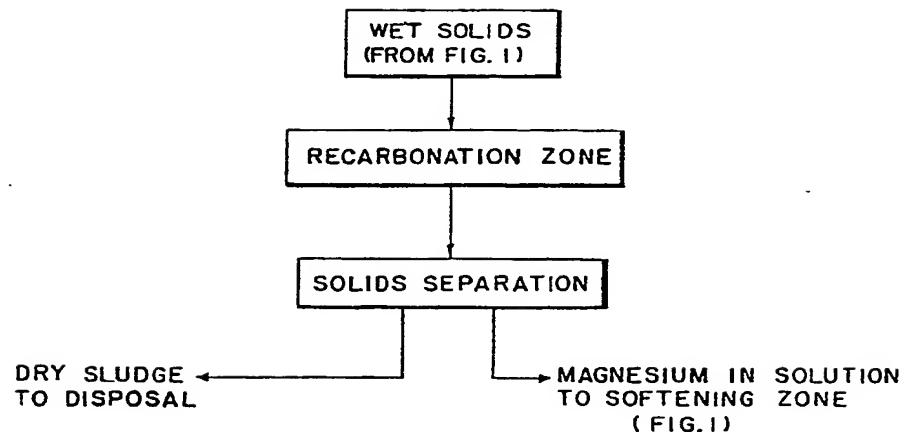


FIG. 2

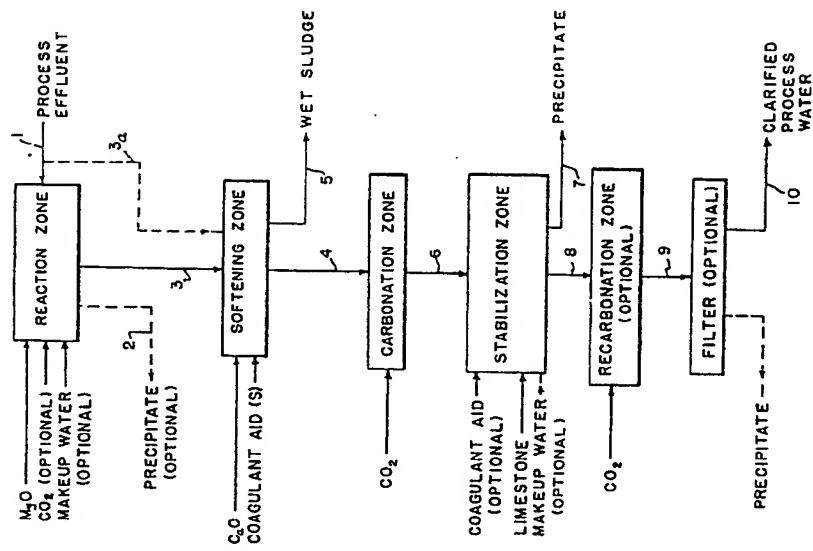


FIG. 1

FIG. 2

